

# Preparation and Properties of Paraffin/Polyurethane Foams Composite with Flame Retardant as Thermal Energy Storage Materials

Liang Zhao<sup>a</sup>, Gang Wang, Xiangchen Fang, Jianfeng Sun, Chunyan Yang

Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, Fushun, 113001, China

<sup>a</sup>zhliang2003@163.com

**Abstract**-Thermal energy storage plays an important role in energy conservation, and can be applied in many areas. Paraffin/polyurethane foams composite with flame retardant as thermal energy storage materials were prepared by absorbing paraffin in honeycomb structure of polyurethane rigid foams. These composites provide a new energy saving materials, which can be used for building heating/cooling systems, and the composites can also enhance the thermal comfort for residents. In the composites, paraffin was used as the phase change material (PCM), polyurethane (PU) rigid foams acting as the supporting material, or as nano-structured calcium carbonate (nano-CC) and red phosphorus (RP) acting as the flame retardant. The thermal properties, such as phase change temperature and latent heat, were investigated by a differential scanning calorimeter (DSC). Chemical structure, micro-structure and flame retardant properties of paraffin/ polyurethane foams composite were determined by FT-IR, SEM and limited oxygen index (LOI) tester, respectively. The SEM results showed that paraffin was well dispersed in honeycomb structure of polyurethane rigid foams. The DSC results indicated that the composites melt at 80.3°C with a latent heat of 25.8kJ/kg when the mass percentage of paraffin in the composites was 16.7%. The LOI results showed that nano-CC and RP decreased the flammability of the composites.

**Keywords**-Polyurethane Foams; Paraffin; Phase Change Materials; Flame Retardant; Thermal Energy Storage

## I. INTRODUCTION

Today's storage problems and costly energy resources have become the primary force driving intensive development of phase change materials (PCMs) [1-6]. In latent heat storage system, thermal energy is stored in PCMs during a melting process while it is recovered during a freezing process. PCMs have received attention for various applications in solar heating systems [7-9], and building energy conservation [10-12]. Polyurethane rigid foams have been widely used for thermal insulation as the ultimate energy savers. Compared with other insulation materials, they are highly competitive. The air trapped within the honeycomb like structure developing passive insulation characteristics of foam in addition to polyurethanes' heat absorption capacity. They are also chlorofluorocarbon free and recyclable [13]. The attempt of applying PCMs in polyurethane foams to improve their thermal performance was developed in 1990s; the foams containing PCMs can improve the heat-insulating ability [14, 15]. According to different phase change temperatures of PCMs, the polyurethane foams can gain various applications, such as building energy conservation, energy saving technology for crude oil pipeline transportation. However, due to the chemical constitution of PU and paraffin, the composites are easily flammable whereas a decrease in the flammability becomes very important.

The fabrication of paraffin/polyurethane foams composite was presented in details. The effects of thermal properties and flame retardant properties of paraffin/polyurethane foams composite were investigated.

## II. EXPERIMENTAL

### A. Materials

Polyurethane foam mixed materials (stuff A: mixture of polyether polyol, foaming agent and so on. Stuff B: isocyanate) were purchased from Yantai Wanhua Co. Ltd., Shandong Province, China. The producer proposed weight ratio: stuff A:stuff B = 100:50, stuff temperature: 20-25°C, mold temperature: 55°C. The nano structured calcium carbonate (nano-CC) and red phosphorus (RP) were supplied by Jiangxi Huaming Co. Ltd., Jiangxi Province, China. Paraffin was made in FRIPP with the paraffin melting point 80-86°C, melting latent heat of 174.4kJ/kg.

### B. Fabrication of Paraffin/Polyurethane Foams Composite with Flame Retardant

The predetermined masses of stuff A, paraffin and flame retardant were added in a beaker and mixed vigorously with strong stirring for 30s to obtain a formulated mixture. The predetermined masses of stuff B were then added into the same beaker with strong stirring for 60s. The resulted mixture was left undisturbed for about 5 min allowing the formation and growth of the foam. Then it was moved and kept in an oven at 50°C. Four kinds of paraffin/polyurethane foams composite were obtained, denoted PCM-1, PCM-2, PCM-3, and PCM-4. The compositions of paraffin, PU, and flame retardant in the composites are listed in Table I.

TABLE I THE COMPOSITIONS OF PARAFFIN, PU AND FLAME RETARDANT IN THE COMPOSITES

Samples	Compositions (in mass portions)
PCM-1	50g PU
PCM-2	50g PU + 10g Paraffin
PCM-3	50g PU + 10g Paraffin + 12g nano-CC
PCM-4	50g PU + 10g Paraffin + 12g nano-CC + 3g RP

### C. Characterization of Paraffin/Polyurethane Foams Composite with Flame Retardant

The thermal properties of composites was obtained by using a differential scanning calorimeter (STA 449C Netzsch) at 5°C/min under a constant stream of nitrogen at a flow rate of 20 ml/min. The structural analysis of composites was carried out using a FT-IR spectrometer. The FT-IR Spectra were recorded on a Nicolet 6700 from 500 to 4000 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> using KBr pellets. Microstructures of the PU and composites were observed by using a SEM (Jeol 7500F, Japan) at room temperature. The flame retardant properties of composites was determined by limited oxygen index tester (JF-3, Jiangning Analysis Instrument Factory, China).

## III. RESULTS AND DISCUSSION

### A. FT-IR Analysis of Paraffin/Polyurethane Foams Composite

FT-IR spectra of the synthesized foams, namely PCM-1, PCM-2 and paraffin are presented in Fig. 1. The spectrum of PCM-1 presents all the distinctive bands of the polyurethane foams. The spectra of experimental groups are compared with that of PCM-1 and paraffin. The band of -OH stretching vibration at 3435-3352 cm<sup>-1</sup> is associated with the free H<sub>2</sub>O, -OH groups of non-bonded polyol or -OH groups within the foams structure. Peaks related to -CN and -C=O at 2271 and 1708 cm<sup>-1</sup> observed in the spectrum of PCM-1 disappear in the spectrum of PCM-2. This indicates incompleteness of PU chain arising from the addition of a secondary material into the structure. The intensity increases in peaks for -CH<sub>2</sub> at 2955.9 and 2917.8 cm<sup>-1</sup> of PCM-2 is associated with capturing paraffin.

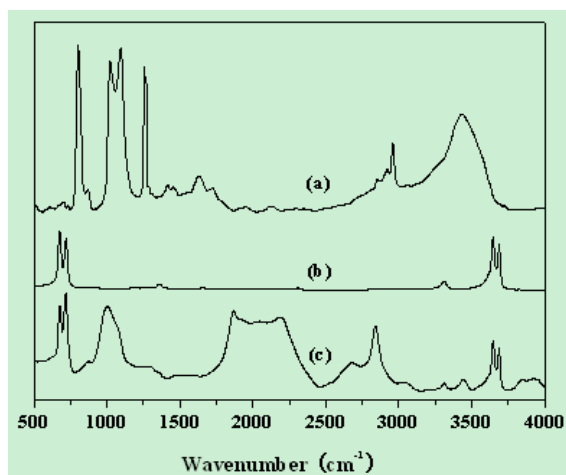


Fig. 1 FT-IR spectra of (a) PCM-1, (b) paraffin and (c) PCM-2

These characterized peaks are the evidence of a successful paraffin trapping in PU foams [16, 17]. It is meanwhile found that there is no shift in the absorption peaks of composites when compared with the spectra of paraffin. This result indicates that there is no chemical interaction between the functional groups of paraffin and PU.

### B. SEM Photos of Paraffin/Polyurethane Foams Composite

SEM photos of PU foams and composites are shown in Fig. 2. Fig. 2 (b) clearly illustrates some paraffin micelles distributing in PU foams. The excellent honeycomb structure obtained during foam formation made considerable amount of

still air trapping possible, and effectively prevented the leakage possibility of paraffin [18,19].

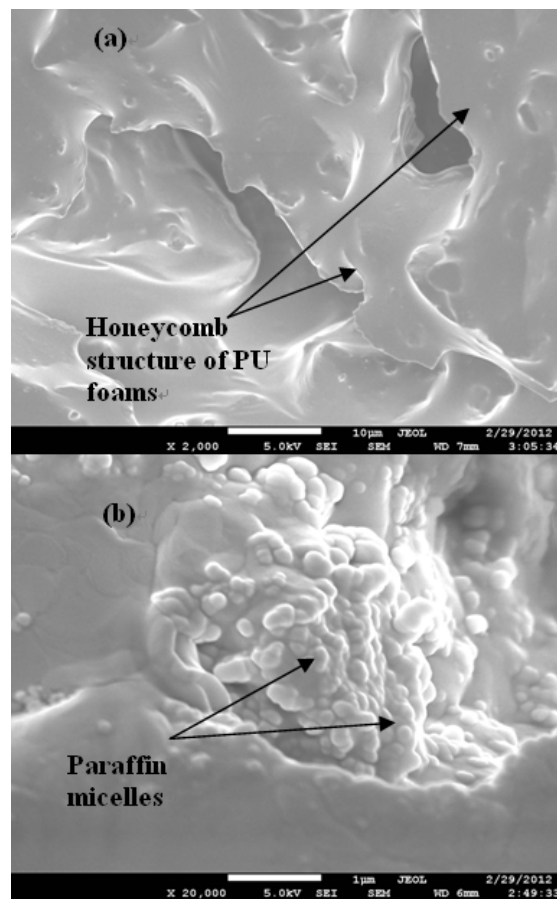


Fig. 2 SEM photos of (a) PU foams and (b) PCM-2

### C. The Thermal Properties of Paraffin/Polyurethane Foams Composite

Fig. 3 illustrates DSC curves of PU foams with paraffin and flame retardant. Compared with the pure PU foams, paraffin/PU foams composite has endothermic peak in the process of heating in the point of 80.3°C, melting latent heat of 25.8kJ/kg. As shown in Table II, flame retardant has no significant influence to the latent heat. After the addition of paraffin with different melting temperatures, different paraffin/PU foams composite with various phase change temperatures can be gained.

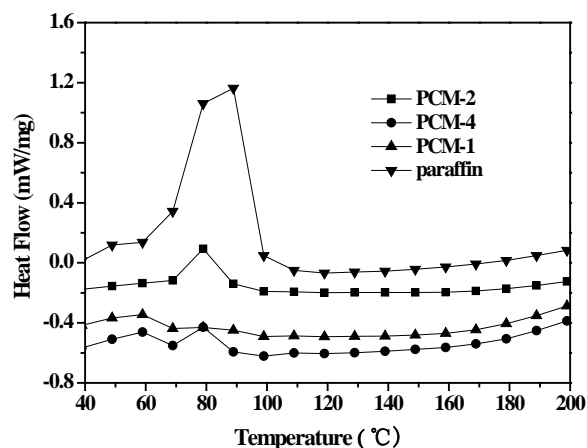


Fig. 3 The melting DSC curves of paraffin and PCMs

TABLE II DSC DATA OF THE PARAFFIN AND PCMS

Sample	Solid-liquid melting	
	Temperature (°C)	Latent heat (kJ/kg)
paraffin	86.4	174.4
PCM-1	—	—
PCM-2	80.3	25.8
PCM-4	79.6	24.9

#### D. Flame Retardant Properties of Paraffin/ Polyurethane Foams Composite

The calculated LOI values of the prepared composites are presented in Table III. Table III shows that the LOI of the pure PU foams is only 16%. It is obvious that the addition of the flame retardant system into PU could improve the LOI value effectively and therefore promote the fire resistance.

TABLE 3 LOI VALUES OF COMPOSITES WITH AND WITHOUT THE FLAME RETARDANT SYSTEM

Sample	Compositions of flame retardant	LOI (%)
PCM-1	—	16
PCM-2	—	15
PCM-3	nano-CC	24
PCM-4	nano-CC + RP	27

The enhanced fire resistance of the flame retardant composites could be explained by the fire suppression mechanism of nano-CC and RP. The thermal decomposition of CC is an endothermic process, which can release CO<sub>2</sub> to decrease temperature and dilute oxygen and flammable gases concentrated near the flame[20]. The decomposition product CaO is a fine flame material used as a retardant. The incorporation of RP into composites also improves the thermo-oxidative stability [21]. In a word, nano-CC and RP give a synergetic flame retarding effect to the composites.

#### IV. CONCLUSIONS

The preparation and properties of paraffin/PU foams composite with flame retardant are reported. Paraffin was used as PCM for thermal energy storage, and PU foams acted as the supporting material for improving the thermal stability of the composites. Nano-CC and RP were added in the composites in order to decrease the flammability of the composites. Paraffin was well dispersed in the honeycomb structure of the PU foams by capillary and surface tension forces, and the leakage of melted paraffin from the composites can be prevented even when it was heated above the melting temperature of the paraffin. As the mass percentage of paraffin in the composites was 16.7%, the composites melt at 80.3°C with a latent heat of 25.8kJ/kg. The addition of nano-CC and RP in the composites improved the thermal stability and increased the LOI values from 16% to 27%.

#### ACKNOWLEDGEMENTS

The authors thank the China Petroleum & Chemical Corporation Foundation (Grant no. 031109) for financial

support of this research. The authors also wish to thank reviewers for kindly giving revising suggestions.

#### REFERENCES

- [1] K. Kaygusuz, T. Ayhan, "Exergy analysis of solar-assisted heat-pump systems for domestic heating", *Energy*, 18,1077-1085, 1993.
- [2] M.N. Roxas-Dimaano, T. Watanabe, "The capric and lauric acid mixture with chemical additives as latent heat storage materials for cooling application", *Energy*, 27, 869-888, 2002.
- [3] H. Benli, A. Durmus, "Performance analysis of a latent heat storage system with phase change material for new designed solar collectors in greenhouse heating", *Solar Energy*, 83, 2109-2119, 2009.
- [4] B. Zalba, J. M. Marin, L.F. Cabeza, H. Mehling, "Review on thermal energy storage with phase change materials", *heat transfer analysis and applications*, *Applied Thermal Engineering*, 23, 251-283, 2003
- [5] M. Kenisarin, K. Mahkamov, "Solar energy storage using phase change materials", *Renewable and Sustainable Energy Reviews*, 11, 1913-1965, 2007.
- [6] F. Agyenim, N. Hewitt, P. Eames, M. Smyth, "A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTES)", *Renewable and Sustainable Energy Reviews*, 14, 615-628, 2010.
- [7] A. Shukla, D. Buddhi, R.L. Sawhney, "Solar water heaters with phase change material thermal energy storage medium: a review", *Renewable and Sustainable Energy Reviews*, 13, 2119-2125, 2009.
- [8] A. Koca, H.F. Oztup, T. Koyun, Y. Varol, "Energy and exergy analysis of a latent heat storage system with phase change material for a solar collector", *Renewable Energy*, 33, 567-574, 2008.
- [9] W. Saman, F. Bruno, E. Halawa, "Thermal performance of PCM thermal storage unit for a roof integrated solar heating system", *Solar Energy*, 78, 341-349, 2005.
- [10] A. Pasupathy, R. Velraj, "Effect of double layer phase change material in building roof for year round thermal management", *Energy Building*, 40, 193-203, 2008.
- [11] V.V. Tyagi, D. Buddhi, "PCM thermal storage in buildings: a state of art", *Renewable and Sustainable Energy Reviews*, 11, 1146-1166, 2007.
- [12] A. Pasupathy, L. Athanasius, R. Velraj, R.V. Seeniraj, "Experimental investigation and numerical simulation analysis on the thermal performance of a building roof incorporating phase change material (PCM) for thermal management", *Applied Thermal Engineering*, 28, 556-565, 2008.
- [13] A. Demharter, "Polyurethane rigid foam: a proven thermal insulating material", *Cryogenics*, 38, 113-117, 1998.
- [14] Y.G. Bryant, D.P. Colvin, "Moldable foam insole with reversible enhanced thermal storage properties", *US Patent* 5,499,460, 1996.
- [15] R.L. Everitt, P.R. Harrison, R.V. Onufrak, "Energy absorbing, water blown, rigid polyurethane foam", *US Patent* 6,028,122, 2000.
- [16] R. Zhang, H. Xu, Y. Zhang, "Preparation, physical property and thermal physical property of phase change microcapsule slurry and phase change emulsion", *Solar Energy Materials & Solar Cells*, 80, 405-416, 2003.
- [17] K. Choi, G. Cho, P. Kim, C. Cho, "Thermal storage/release and mechanical properties of phase change materials on polyester fabrics", *Textile Research Journal*, 74, 292-297, 2004.
- [18] N. Sarier, E. Onder, "Thermal characteristics of polyurethane foams incorporated with phase change materials", *Thermochimica Acta*, 454, 90-98, 2007.
- [19] G.Y. Fang, H. Li, Z. Chen, X. Liu, "Preparation and properties of palmitic acid/SiO<sub>2</sub> composites with flame retardant as thermal energy storage materials", *Solar Energy Materials & Solar Cells*, 95, 1875-1881, 2011.
- [20] P.A. Larcey, J.P. Redfern, G.M. Bell, "Study on magnesium hydroxide in polypropylene using simultaneous TG-DSC", *Fire and Materials*, 19, 283-285, 1995.
- [21] Z.Z. Wang, G.S. Wu, Y. Hu, Y. Ding, K.L. Hu, W.C. Fan, "Thermal degradation of magnesium hydroxide and red phosphorus flame retardant polyethylene composites", *Polymer Degradation and Stability*, 77, 427-434, 2002.



**Liang Zhao** (China, 1980-) majored in catalytic materials and gained a doctor degree of industrial catalysis in Dalian University of Technology at 2010, which was in Dalian city, Liaoning province, China.

He is working for Fushun Research Institute of Petroleum and Petrochemicals of SINOPEC since July 2010, which was in Fushun city, Liaoning province, China. And also, he is majoring in thermal energy storage, the published articles were

as follows:

[1] Liang Zhao, Hongbo Wang, Min Liu, et al. "Shape-selective methylation of 2-methylnaphthalene with methanol over hydrothermal treated HZSM-5 zeolite catalysts", Chem. Eng. Sci., 63(21): 5298-5303(2008).

[2] Liang Zhao, Xinwen Guo, Min Liu, et al. "Methylation of 2-methylnaphthalene with methanol over  $\text{NH}_4\text{F}$  and Pt modified HZSM-5 catalysts", Chin. J. of Chem. Eng., 18(5):742-749(2010).

[3] Liang Zhao, Ruiying Ma, Xianglan Meng, et al. "Characterization and preparation of paraffin/modified inorganic porous materials composites as building energy storage materials", Adv. Mater. Res. 450-451:1419-1424(2012).

**Gang Wang** (China, 1968-) majored in petroleum refining engineering and gained a doctor degree of physical chemistry in Dalian Institute of Chemical

Physics, Chinese Academy of Science at 2008, which was in Dalian city, Liaoning province, China.

He is working for Fushun Research Institute of Petroleum and Petrochemicals of SINOPEC, which was in Fushun city, Liaoning province, China. Also, he is a professor and majors in petroleum refining and thermal energy storage now.

**Xiangchen Fang** (China, 1960-) majored in petroleum refining engineering. He is working for Fushun Research Institute of Petroleum and Petrochemicals of SINOPEC, which was in Fushun city, Liaoning province, China. Also, he is a professor and majors in petroleum refining and thermal energy storage now.

**Jianfeng Sun** (China) majored in thermal energy storage. He is working for Fushun Research Institute of Petroleum and Petrochemicals of SINOPEC, which was in Fushun city, Liaoning province, China. Also, he is a senior engineer and majors in thermal energy storage now.

**Chunyan Yang** (China) majored in thermal energy storage. She is working for Fushun Research Institute of Petroleum and Petrochemicals of SINOPEC, which was in Fushun city, Liaoning province, China. Also, she is an engineer and majors in thermal energy storage now.